



## Microwave-assisted catalytic biomass pyrolysis: Effects of catalyst mixtures

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## ABSTRACT

This paper studied the catalytic effects of mixtures of different catalysts (*i.e.*, K<sub>3</sub>PO<sub>4</sub> “KP”, Bentonite “Bento” and Clinoptilolite “Clino”) on biomass catalytic pyrolysis compared to the single catalyst under microwave heating and thermogravimetric analyzer (TGA). Since some catalysts can promote microwave absorption while others show promising catalytic effects, it is possible to use mixtures of catalysts to improve high microwave heating rate and simultaneously catalyze biomass pyrolysis reactions. 10K<sub>3</sub>PO<sub>4</sub>/10Bentonite (10 wt.%KP + 10 wt.% Bento) catalyst mixture increased the mass loss rate by 85% and 45% at 100 and 25 °C/min, respectively, compared to switchgrass without catalyst. The highest microwave heating rates for torrefaction (110–260 °C) and pyrolysis stages (260–400 °C) were found for the catalyst mixtures, with the highest being achieved by 10KP/10Bento. It was also found that the catalyst mixtures affected the type of coke deposited on catalyst surfaces during pyrolysis, which plays an important role on determining the microwave heating rate under microwave catalytic pyrolysis by affecting the dielectric properties of the bed material and then microwave absorption. Oxygenated-coke deposited on catalyst surfaces reduces the microwave heating rate markedly, while graphitic-coke increases the microwave heating rate considerably. Finally, catalyst combinations improved the catalytic performance significantly and reduced the catalyst loads which in turn will reduce the production cost of bio-oil and biochar from microwave-assisted catalytic pyrolysis.

## 1. Introduction

Pyrolysis is a thermochemical decomposition of material under inert conditions that can produce multiple products over a very short reaction time, including biochar, bio-oil and noncondensable gases [1,2]. Pyrolysis is considered as one of the successful routes that can produce bio-oil from wood and agricultural wastes [3]. Fast pyrolysis has been explored mainly for the production of bio-oil, with a maximum yield > 70 wt.% [1,4]. However, there are many challenges associated with this technology such as the poor quality of the produced bio-oil (*i.e.*, high oxygen content, high acidity and viscosity, and heavy components) and the heterogeneous nature of biomass feedstock [4,5]. Slow pyrolysis produces bio-oil with high water content due to dehydration reactions which are favoured at low temperatures (< 325 °C) and slow heating rate [6]. While, high heating rates result in high bio-oil yield and high biochar quality [1,4,5]. More efficient or targeted heating method such as microwave heating and effective catalysts have been explored to improve the qualities of bio-oil and biochar [7].

Fundamental studies for the kinetics of the pyrolysis reactions will help to better understand the reaction pathways and predict the

pyrolysis behaviour of biomass materials at different operating conditions so that more efficient pyrolytic reactors can be designed [2,3]. Biomass pyrolysis is a complex process, which mostly cannot be described by a single step reaction model. In addition, lignocellulosic materials contain at least three main components which are cellulose, hemicellulose and lignin, which decompose differently, as reflected by partially overlapping peaks in the mass loss rate curves, and the deconvoluted peaks can be used to study the kinetics for each pseudo-component [2,3]. It is well known that heat transfer and mass transfer play important role on determining pyrolysis product distribution and the quality of products by affecting the extent and selectivity of secondary reactions of primary vapours [1,2,4]. Many analytical techniques have been used to provide good understanding of formation characteristics and kinetics of the three main components (cellulose, hemicellulose and lignin) in the pyrolysis product, such as TGA coupled with GC/MS, Pyroprobe (Py-GC/MS) and micro fluidized beds [2,4,5].

Catalytic pyrolysis has also been explored extensively for improving the quality of bio-oil and noncondensable gases. Many catalysts including natural and synthetic zeolites, and natural clays (bentonite, kaoline, cambrian clays, mergel clays, sepiolite and attapulgite) have

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been investigated [8,9]. It was found that bentonite reduced fractions of heavy compounds in bio-oil and raised bio-oil yield compared with other natural clays and synthetic zeolites [11]; while, the stability of bio-oil organic fraction was also improved after accelerated aging tests [10].

Microwave-assisted pyrolysis for different biomass materials has been explored as an effective method to improve the quality of bio-oil, biochar and syngas [6,11,12]. Moreover, the porosity of biochars produced from microwave-assisted pyrolysis is higher than those produced from conventional pyrolysis. In microwave heating, particles are directly heated. As a result, heterogeneous reactions are favoured in microwave heating compared to conventional heating, and the higher heating rate might affect pore structure of biochar [11,12]. It is reported that biochars produced from microwave-assisted pyrolysis have higher surface area and pore volume than that from conventional heating [7,13,14]. However, due to poor absorption of microwave by dry biomass, microwave absorbers are often added to increase the microwave absorption rate, and thus accelerate the heating rate to reach pyrolysis temperatures at reduced microwave power requirement [6,7,15].

$K_3PO_4$ , clinoptilolite and bentonite have been tested for catalytic pyrolysis under microwave heating and showed better performance as catalysts and improved the quality of bio-oil by reducing acidity, viscosity and producing aromatic compounds and other hydrocarbon products [16]. Furthermore, these catalysts also improved the quality of the produced biochar by increasing the cation exchange capacity (CEC), surface area and increasing nutrients content [17]. In addition, it was found that biochars produced from mixing  $K_3PO_4$  and clinoptilolite or bentonite with biomass showed synergistic effects on reducing toxicity and uptake of heavy metals (i.e., Pb, Ni and Co) due to the predominance of different immobilization mechanisms and also increased the plant productivity grown in a soil contaminated with heavy metals [18]. In view that the benefits of spent catalysts as a natural fertilizer and soil conditioner, it is not necessary to separate and regenerate or recycle the spent catalyst from biochar product, although its economic feasibility still needs to be evaluated in the future based on data from pilot continuous production process.

Coke deposition is a major concern for catalyst deactivation which reduces catalyst activity and affect pyrolysis products distribution [14,18,19]. It is known that oxygenated coke has very low microwave absorption ability compared to graphitic carbon and graphite [21]. Coke strongly adsorbs on the active sites, and blocks catalyst pores entrance. Coke forms at low temperatures ( $< 350^\circ C$ ) mainly through vapour condensation and repolymerization [19,21]. Coke can form from the oxygenated volatile intermediates and the dehydrated species [22,23,24].

It was also found from our previous studies that  $K_3PO_4$  possesses good microwave absorption but inhibited the devolatilization of hemicellulose significantly, leading to increase in the catalytic coke yield compared to other samples [16]. Bentonite, on the other hand, has a high thermal conductivity, does not inhibit hemicellulose decomposition, but possesses poor microwave absorption. Thus, it is expected that mixing the two catalysts can potentially increase the microwave absorption rate and reduce formation of oxygenated coke type that can further affect microwave absorption. It was previously reported that the synergistic effects for catalysts combinations in terms of increasing microwave heating rates were due to exothermic reactions that can be triggered by using catalyst mixtures [16]. Thus, in order to study the catalytic effects of catalyst mixtures on biomass pyrolysis, the effect of catalyst mixtures on microwave heating rates should be decoupled by maintaining a similar heating rate, which cannot be achieved under microwave heating. Therefore, differential thermogravimetry analysis (DTA) will be used to measure the heat flow at constant heat rates for switchgrass (SG) and SG mixed with different catalysts or different catalyst mixtures.

In order to elucidate the effect of catalyst mixtures on increasing the

microwave heating rate, the effect of microwave heating rate should be decoupled from the effect of catalyst activity by maintaining at similar heating rates. Thus, the aim of this study is to understand the synergistic effects of catalyst combinations on increased microwave heating and biomass decomposition rates. It is hypothesized that the type of coke deposited on catalyst surfaces can play an important role on influencing microwave absorption, which determines microwave heating rate of biomass catalytic pyrolysis. To understand the effect of catalyst and catalyst mixture on coke formation, coke deposited on catalyst particles is sampled and characterized. Thus, the aim of this study is to understand the synergistic effects of catalyst combinations on increased microwave heating and biomass decomposition rates. These results can then be used for designing and optimizing the microwave reactors for biomass catalytic pyrolysis.

## 2. Materials and methods

### 2.1. Microwave and TGA catalytic pyrolysis

Switchgrass from Manitoba, Canada, was used in this study for its bioenergy application potential. Bentonite ( $Al_2O_3 \cdot SiO_2 \cdot 2H_2O$ ) and  $K_3PO_4$  (Potassium Phosphate Tribasic, reagent grade,  $\geq 98\%$ ) were purchased in powder form from Sigma-Aldrich, Canada Co. Commercial grade clinoptilolite ( $(K,Ca,Na)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 6H_2O$ ) was purchased from Bear River Zeolite Co, USA. A total of 20.0 g of pure switchgrass (300–600  $\mu m$ ) or switchgrass mixed with different loads (10, 20 and 30 wt.%) of natural zeolite (clinoptilolite), bentonite or  $K_3PO_4$  ( $\leq 50 \mu m$ ) was pyrolyzed in a tubular reactor. Different catalysts were mixed at different fractions in order to investigate the effect of catalyst mixtures on microwave heating and biomass catalytic pyrolysis. Because of the poor microwave absorption rate of pure switchgrass (maximum temperature  $< 160^\circ C$  after 30 min of microwave irradiation), no pyrolysis reaction can be triggered to produce biochar from switchgrass without the addition of catalyst. To elucidate the catalytic effect, SiC, which is a chemically inert microwave absorber for accelerating microwave heating, is used to benchmark the non-catalytic microwave pyrolysis for revealing the catalytic effects of the three selected catalysts on bio-oil properties and biochar properties. More information about the microwave reactor and experimental setup can be found in our previous work [16].

The produced biochars from microwave pyrolysis contained catalysts or catalysts mixtures, which were screened to separate the biochars from spent catalysts with the deposited catalytic coke. The samples of spent catalysts with the deposited catalytic coke were then characterized using temperature programmed oxidation (TPO) and Raman spectroscopy to investigate the different functional groups on the catalyst surfaces, and the dielectric properties of those samples were measured to study the effect of deposited catalytic coke type on microwave heating and solid yield.

In order to measure heat flow at constant heating rates for SG and SG mixed with different catalysts or different catalyst mixtures, Thermogravimetric analysis (TGA) of the samples was conducted using SDT Q600 TGA-DTA with a nitrogen flow rate of 100 mL/min. Switchgrass was sieved to small particles (100–150  $\mu m$ ) to obtain a low Biot number ( $< 0.01$ ) in order to reduce the internal heat and mass transfer.  $K_3PO_4$ , clinoptilolite and bentonite with particles size  $\leq 50 \mu m$  were mixed at 30 wt.% for single catalyst, and 10/10 wt.% for catalyst combinations. The sample was loaded into a crucible made of alumina and the weight was recorded every 0.5 s with the accuracy of the balance being 0.0001 mg, and the experiments were performed at heating rates of 25 and 100  $^\circ C/min$ . The temperature programmed oxidation (TPO) procedure was performed under air at a heating rate of 20  $^\circ C/min$ .

**Table 1**

Heating rates for switchgrass mixed with different catalysts or activated carbon at different heating stages under microwave-assisted pyrolysis.

Sample	Abbreviations	Heating rate, °C/min (110 – 260 °C, torrefaction)	Heating rate, °C/min (260 – 400 °C, pyrolysis)	Overall heating rate, °C/min (110 – 400 °C)
10 wt.% clinoptilolite	10Clino	145	9	19
20 wt.% clinoptilolite	20Clino	169	10	21
30 wt.% clinoptilolite	30Clino	391	39	81
10 wt.% K <sub>3</sub> PO <sub>4</sub>	10KP	173	10	20
20 wt.% K <sub>3</sub> PO <sub>4</sub>	20KP	380	38	79
30 wt.% K <sub>3</sub> PO <sub>4</sub>	30KP	219	9	19
10 to 30 wt.% Bentonite	Bento	Maximum temperature < 200 °C	–	–
20 wt.% activated carbon	20AC	265	22	46

### 3. Results and discussion

#### 3.1. Effects of catalysts mixtures on microwave heating behaviour

##### 3.1.1. Microwave heating control and mechanism

K<sub>3</sub>PO<sub>4</sub> is an ionic compound that possesses good microwave absorption ability. Bentonite is a natural aluminum phyllosilicate (mostly montmorillonite) with low microwave absorption ability at room temperature, but can serve as a heat-carrier due to its high thermal conductivity (1.15, W/m K) compared to the low thermal conductivity for switchgrass (0.10, W/m K) [11,25], leading to more uniform heating of SG. However, microwave heating rate is mainly determined by the microwave absorption rate rather than thermal conductivity. This is confirmed by the data in Table 1 in which mixing bentonite at different loads (10–30 wt.%) with switchgrass did not significantly increase the microwave heating rate of switchgrass, compared to K<sub>3</sub>PO<sub>4</sub> or clinoptilolite, with the maximum temperatures recorded for bentonite mixed with switchgrass being well below 200 °C.

A possible mechanism for microwave heating of biomass premixed with a microwave absorber is that the microwave radiation is first absorbed by microwave absorbing material and then the absorbed energy is transferred to biomass through heat conduction [14]. Under microwave catalytic pyrolysis, catalysts that possess high microwave absorption ability will be heated faster than biomass particles and then will serve as a heating medium to transfer heat to biomass particles via mostly conduction (solid-solid contact heat transfer). Released vapours from biomass particles will then diffuse into catalyst pores where they are catalytically cracked (solid-vapour interactions).

##### 3.1.2. Effect of catalysts and catalysts mixtures on microwave heating behaviour of switchgrass

The microwave heating behaviour of pure switchgrass, switchgrass with different loads of catalysts, and their combinations are presented in our previous work [16]. Based on the heating behaviour for different samples under microwave catalytic pyrolysis (Fig. 1), the whole process can be divided into three main stages; drying (25–110 °C), heating and torrefaction (110–260 °C, depolymerization, and partial devolatilization) and pyrolysis (~260–400 °C, devolatilization).

Tables 1 and 2 show the microwave heating rates for switchgrass mixed with different catalysts or their combinations at different stages (torrefaction and pyrolysis) and total heating rates under microwave-assisted catalytic pyrolysis. It can be seen that the heating rate is mostly affected between 260 and 400 °C (pyrolysis stage) in which the heating rate with catalyst mixtures is much higher than what is expected from the simple combination of the two catalysts. In general, the microwave heating rate at the pyrolysis stage (260–400 °C) is much lower than at the torrefaction stage (110–260 °C) and the lowest was found for sample 30KP (Fig. 1), likely due to the occurrence of endothermic biomass pyrolysis reactions. However, the highest heating rate at pyrolysis stage was found for the catalyst mixtures, with the highest value for sample 10KP/10Bento. It is noted that adding bentonite only to switchgrass at different loads up to 30 wt.% did not increase the

microwave heating rate, with the recorded maximum temperatures well below 200 °C. This further confirms the existence of a synergistic effect of catalyst mixtures on increasing microwave heating rates.

Increasing the percentage of clinoptilolite increased the heating rate at both the torrefaction and pyrolysis stage. However, the addition of K<sub>3</sub>PO<sub>4</sub> exhibited different trends. As shown in Table 1, heating rate increased when percentage of K<sub>3</sub>PO<sub>4</sub> increased from 10 to 20%, but decreased when the percentage further increased from 20 to 30%. Fig. 1 further shows that the sample with 30% K<sub>3</sub>PO<sub>4</sub> load gave the fastest initial temperature increase at temperature < 230 °C, which is supported by the increased microwave absorption rate, but the trend changed noticeably beyond 250 °C and it took the longest time for the sample to reach 400 °C. It has also been reported that higher percentage of K<sub>3</sub>PO<sub>4</sub> inhibits the devolatilization of hemicellulose to create organic volatile compounds, leading to higher solid yield using Pyroprobe at a very high heating rate > 10,000 °C/min [26]. Thus, it is speculated that 30 wt.% K<sub>3</sub>PO<sub>4</sub> shifted the decomposition reactions of hemicellulose, and catalytic coke started to form at lower temperatures. This will be discussed in more details in the following section.

It is noticed in Table 2 that 10KP/10Clino showed a low heating rate at the torrefaction stage but a high heating rate at the pyrolysis stage compared to other single catalysts with different loads. This indicates that the combined catalysts may have strongly influenced biomass pyrolysis reactions. At the pyrolysis stage, many chemical reactions with different reaction pathways and heat of reactions (endothermic or exothermic) take place simultaneously, leading to the formation of different types of catalytic coke on catalyst surfaces. As catalyst particles absorb microwaves and transfer to biomass particles through different heat transfer modes, the microwave absorption of catalyst particles could be affected by the coke deposited on the catalysts surface, which in turn will affect the microwave heating rates of biomass particles.

It was speculated previously that the synergistic effects for catalyst combinations in terms of increased microwave heating rates were due to exothermic reactions triggered by catalysts mixtures [16]. In order to show the effect of catalyst combinations on exothermic reactions, DTA analysis was conducted at different heating rates (25 and 100 °C/min) in a TG unit. It was found that the 10KP/10Bento sample was more endothermic compared to 30KP and SG at different heating rates for temperatures ranging from 200 to 400 °C under TGA (Fig. 2). However, 10KP/10Bento showed the highest microwave heating rate within the same temperature range under microwave heating, compared to other samples. In addition, the heat flow at the decomposition stage from ~280 to 400 °C is almost neutral for SG and other catalysts at different heating rates, but significant fluctuations in the heating rate under microwave heating were observed between 300 and 400 °C which may be caused by the change in microwave absorption (Fig. 2). These findings appear to agree with the reported data in which cellulose decomposition was found to be endothermic while decomposition of hemicellulose and lignin was exothermic between 300 and 400 °C [27], and the overall heat flow associated with decomposition of whole biomass can be neutral at the pyrolysis stage. Furthermore, they

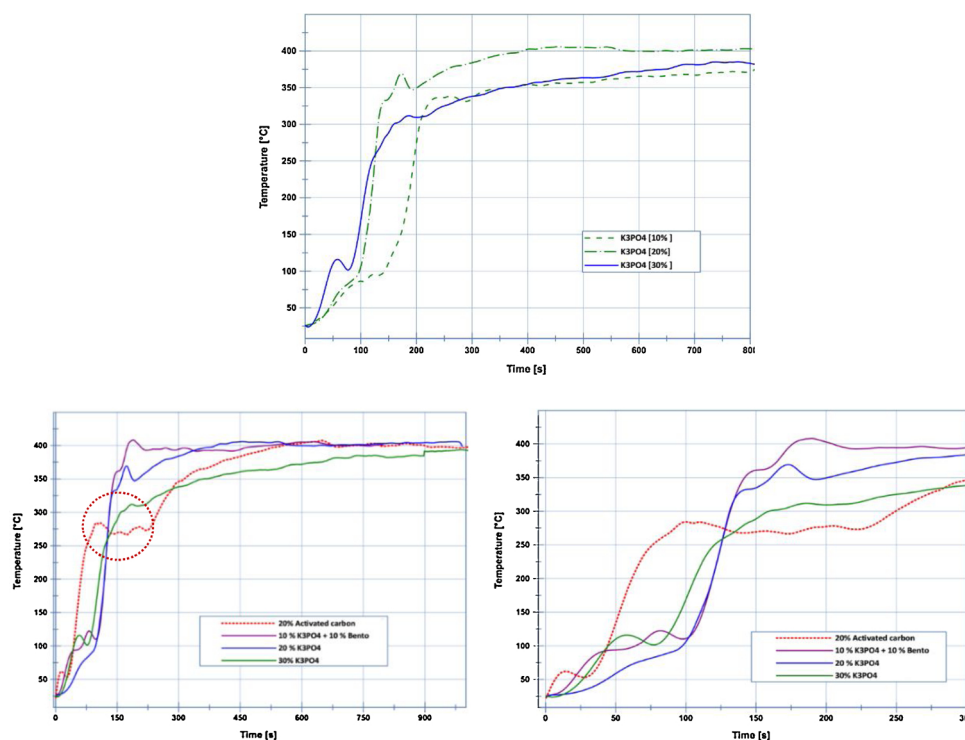


Fig. 1. Temperature rise profiles of  $K_3PO_4$  (KP), and comparison with activated carbon and KP/Bento mixture under microwave catalytic pyrolysis.

suggested that exo/endothermic reactions do not play a major role on affecting the microwave heating behaviour of these samples within the temperature range of 200–400 °C, and the high microwave heating rates observed for the catalyst mixtures were unlikely the result of exothermic decomposition reactions.

Our results on heat flow under TGA and the literature data [27] seem to suggest that the exothermic reactions hypothesis proposed in our previous study cannot be the main cause of the synergistic effects of catalyst mixtures on increasing microwave heating rate [16]. Instead, the change of dielectric properties of catalyst particles caused by deposited coke, which determines microwave absorption ability, may be the major cause of the high microwave heating rate at the microwave catalytic pyrolysis stage.

### 3.1.3. Catalytic behaviour of $K_3PO_4$ under microwave-assisted pyrolysis

The produced bio-oil was further characterized in this study to understand the catalytic mechanism, with the chemical composition of total bio-oil (organic and aqueous phases) produced from SG mixed with SiC and SG mixed with 30%  $K_3PO_4$  under microwave-assisted pyrolysis being analyzed by a GC–MS, with the results shown in Table S1 of Supplementary Material. It was found that  $K_3PO_4$  significantly altered the chemical composition of bio-oil and, as expected, acids, ketones, aldehydes, furans contents were markedly reduced or completely eliminated, while phenolics and other aromatics compounds dramatically increased, compared to SG mixed with SiC. In addition, some hemicellulose derivatives such as 2-Furaldehyde, aldehydes and anhydrosugars were completely eliminated. Table 3 shows the lumped

products composition. Acetic acid was found to be the major acid product from deacetylation of hemicellulose [26]. The primary oxygenated compounds derived from hemicellulose such as acetic acid, acetaldehyde and acetyl are main precursors for catalytic coke formation through decarboxylation and dehydration [28]. There is also 3-folds increase in the phenolic compounds compared to SG mixed with SiC. These findings confirm that potassium has a great inhibitory effect on the primary oxygenated compounds originated from hemicellulose [26].

Potassium is the most influential element on pyrolysis product distribution and is known to promote crosslinking reactions that can result in increased solid yield with exothermic behaviour which also in line with the highest biochar yield from 30KP sample at 1.5 L/min of nitrogen flow [28,29]. The catalytic role of potassium in biomass pyrolysis has shown that it lowers the temperatures of initial and maximum decompositions, promotes the formation of char, gas,  $H_2O$  and phenols, and suppresses the formation of levoglucosan, furans, pyrans, acetol, acids and aldehydes [29,30], reducing the liquid yield markedly [25,31,32]. The significant increase in phenolic compounds using potassium catalyst results from the cleavage of different linkages ( $\beta$ -O-4 aryl ether bond, etc.) in addition to side-chain elimination reactions [25,28]. Furthermore, alkali metals at higher percentages  $\geq 20$  wt.% are shown to promote coke production [6], which may deactivate the catalyst and reduce its microwave absorption efficiency, which in turn may reduce the biomass conversion rate and produce more solid.

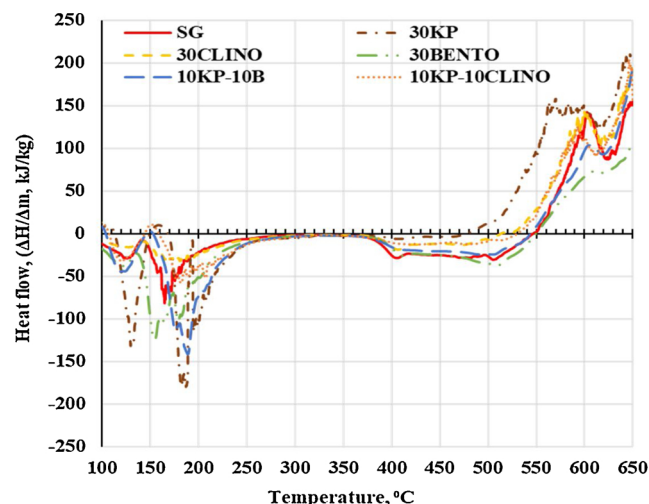
It was also found that potassium promotes coke formation, in line with other studies [28,29]. Proposed mechanisms suggest hydrocarbon

Table 2

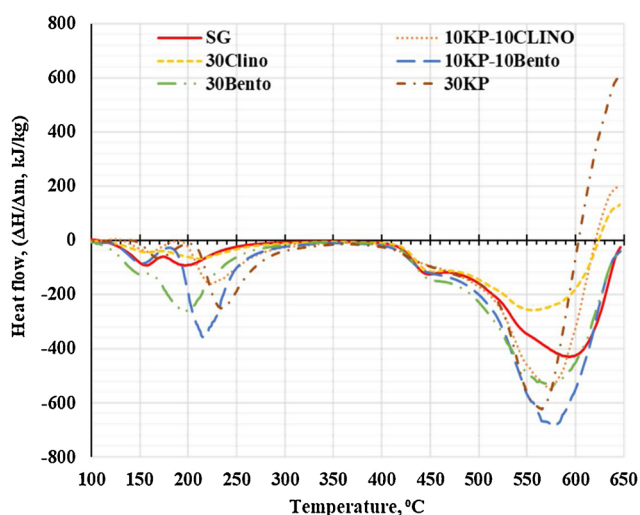
Heating rates for switchgrass mixed with different catalyst mixtures at different heating stages under microwave-assisted pyrolysis.

Sample	Abbreviations	Heating rate, °C/min (110 – 260 °C, torrefaction)	Heating rate, °C/min (260 – 400 °C, pyrolysis)	Overall heating rate, °C/min (110 – 400 °C)
10 wt.% $K_3PO_4$ + 10 wt.% bentonite	10KP/10Bento	409	179	271
10 wt.% $K_3PO_4$ + 20 wt.% bentonite	10KP/20Bento	200	35	73
10 wt.% $K_3PO_4$ + 10 wt.% clinoptilolite	10KP/10Clino	230	141	193





(a)



(b)

Fig. 2. Heat flow for switchgrass (SG) and SG mixed with different catalysts at heating rates of: (a) 25 °C/min and (b) 100 °C/min using TGA-DTA.

molecules chemisorb onto the catalyst surface and then be converted to carbon by a surface reaction [33,34]. Coke strongly adsorbs onto the active sites, and blocks catalyst pore entrance [34]. Coke forms at low temperatures (< 350 °C) mainly through vapour condensation and re-polymerization [20]. The primary oxygenated vapours from hemicellulose such as acetic acid, acetaldehyde and acetyl are main precursors for catalytic coke formation [28]. The catalytic transformation of acetic acid occurs through decarboxylation and dehydration [22,27]. Therefore, the highest biochar yield from 30 wt.%  $K_3PO_4$ , which is up to 53% higher than the control sample, may be caused by the increased secondary carbon formation “catalytic coke”. This is supported by reported data that potassium increased secondary carbon formation

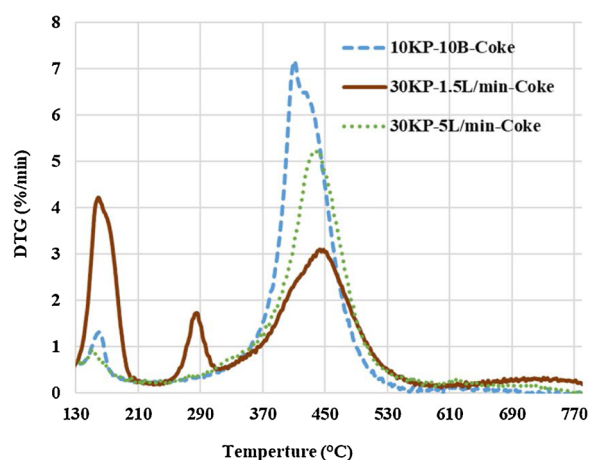


Fig. 3. DTG for different spent catalysts produced from microwave catalytic pyrolysis.

which produces more solid product [6]. To provide support evidence to the proposed catalytic coke mechanism, the properties of catalytic coke need to be analyzed.

### 3.2. Effects of catalysts mixtures on coke formation and coke properties

Fig. 3 shows the DTG curves for the spent 30KP catalyst produced at  $N_2$  flow rate of 1.5 and 5 L/min and spent 10KP/10Bento catalyst produced at  $N_2$  flow rate of 1.5 L/min, obtained following temperature programmed oxidation (TPO) procedure under air at a heating rate of 20 °C/min. The 30KP-1.5L/min sample showed two peaks at low temperatures (160 and 285 °C), while most coke for 30KP-1.5L/min and 10KP/10Bento was removed at temperatures > 360 °C. Catalytic coke removed at temperature < 360 °C called oxygen-containing coke (oxygenated coke), which have a lower combustion temperature, while the catalytic coke removed at temperature > 360 °C may correspond to aromatic hydrocarbons which possess graphitic properties [20], as confirmed later based on the determined functional groups of the spent catalyst.

It was found that the amount of deposited coke on catalyst surfaces for the three samples is similar (about 31 wt.%), which means that the amount of coke deposition is not responsible for the difference in microwave heating rate. Rather, the type of coke deposit with different dielectric properties may be important. DTG curves in Fig. 3 for the three samples showed major peaks at low temperatures (160 and 285 °C) for 30KP-1.5L/min sample with ~51% of coke being removed at temperatures < 360 °C compared to about 19% for 30KP-5L/min. The coke removed at temperatures < 360 °C, called oxygenated coke, has a lower combustion temperature as mentioned before. These findings were also confirmed by the data obtained from Raman Spectroscopy in which disordered carbon/graphitic carbon ratio (D/G ratio) for 30KP-5L/min was 20% lower than the two other samples. This can suggest that more graphitic carbon and less disordered carbon are formed on catalyst surfaces, which will have a high microwave absorption ability, as to be confirmed by measured dielectric properties of the spent catalysts.

Table 3

The lumped product composition of bio-oil (peak area %) produced from SG mixed with SiC and SG mixed with 30 wt.%  $K_3PO_4$  (30KP) under microwave-assisted pyrolysis.

	Acids	Phenolics	Furans	Ketones	Aldehydes	Anhydrosugars
SG + SiC	24.6	11.0	4.81	16.5	1.23	0.63
SG + 30KP	5.95	45.4	1.15	7.12	0	0
Percentage change	−76%	+312%	−76%	−57%	−100%	−100%

It is known that oxygenated coke has very low microwave absorption ability compared to graphitic carbon [21]. Thus, covering catalyst surfaces and active sites with oxygenated coke will reduce microwave absorption and reduce sample heating rate. The spent 30KP-1.5 L/min catalyst having more oxygenated coke and less graphitic coke is expected to have lower dielectric loss than those of 10KP/10Bento and 30KP-5L/min catalysts.

To confirm the effect of coke deposition and the coke type on microwave absorption and microwave heating rate, dielectric properties of the spent catalysts were measured, and the heating rate can be calculated using the following equations:

$$P = \sigma |E|^2 = 2\pi f \epsilon_0 \epsilon'' |E|^2 \quad (1)$$

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \epsilon_0 \epsilon'' |E|^2}{\rho \cdot C_p} \quad (2)$$

Where,  $P$  is the absorbed power per unit volume,  $\lambda_0$  is the microwave wavelength,  $\epsilon'$  dielectric constant,  $\epsilon''$  dielectric loss,  $\sigma$  effective conductivity,  $\epsilon_0$  permittivity of free space,  $E$  is the electric field,  $\frac{\Delta T}{\Delta t}$  is the microwave heating rate,  $\rho$  is material density and  $C_p$  is the specific heat. The ability of a material to absorb microwave radiation is determined by dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ). Dielectric constant depicts the capacity of molecules to be polarized when it is under electric field and represents the efficiency of the material to convert the electromagnetic radiation into heat. Dielectric loss denotes the amount of input microwave energy which is dissipated through heat [20,35].

The heating rate for 30KP-1.5L/min was 219 °C/min, which increased to 327 °C/min for 30KP-5L/min and the biochar yield was reduced by 37% using a high flow rate of  $N_2$  (5 L/min), despite that high flow rate of  $N_2$  (5L/min) will remove more heat from the reaction zone. This illustrates the importance of the dielectric properties of coke deposit on catalyst surfaces in determining the microwave heating rate.

To further confirm the hypothesized effect of oxygenated coke on microwave heating, the coke deposited on the surface of spent catalysts was characterized and semi-quantified using Raman Spectroscopy. As seen in Fig. 4, there are two major peaks and the first peak represents the disordered carbon “D” and the second peak corresponding to graphitic carbon “G”. The figure shows clear differences among those four samples, and to better explain the differences the peaks were deconvoluted into different bands based on the data provided in Table 5 [34].

From the deconvoluted peaks (Figs. 5 and 6) the ratio between the peak areas for D band and G band (D/G) was determined and shown in Table 6. A significant decrease in D/G ratio by 20% was found after  $N_2$  flow rate was increased from 1.5 to 5 L/min for the 30KP sample, which means that less disordered carbon or more graphitic carbon was deposited onto the catalyst surface. This agrees with the trends in their dielectric properties which was considerably higher for 30KP-5 L/min than for 30KP-1.5 L/min. Also, 10KP/10Bento has a lower D/G ratio than 10KP/20Bento by ~18%, which also agrees with the higher heating rate for 10KP/10Bento (179 °C/min) than 10KP/20Bento (35 °C/min) at the pyrolysis stage. 10KP/10Bento showed the highest microwave heating rate as a result of high amount of graphitic carbon that deposited on the catalyst surface, as confirmed by the low D/G ratio, and graphitic carbon possesses very high microwave absorption ability that resulted in increased microwave heating rate particularly during pyrolysis stage (260–400 °C) when coke started to form substantially. In addition, there is a 38% increase in VL band which represents the amorphous carbon, and 33% increase in SL band which refers to aryl-alkyl ether for 10KP/20Bento compared to 10KP/10Bento. These findings may explain the significant decrease in the heating rate for 10KP/20Bento at the pyrolysis stage (260–400 °C) under microwave heating, due to the increase in the amount of amorphous and oxygenated coke deposited on the catalyst surface which in turn increased the D/G ratio, compared to 10KP/10Bento, and it is known amorphous and oxygenated coke is poor in microwave absorption compared to

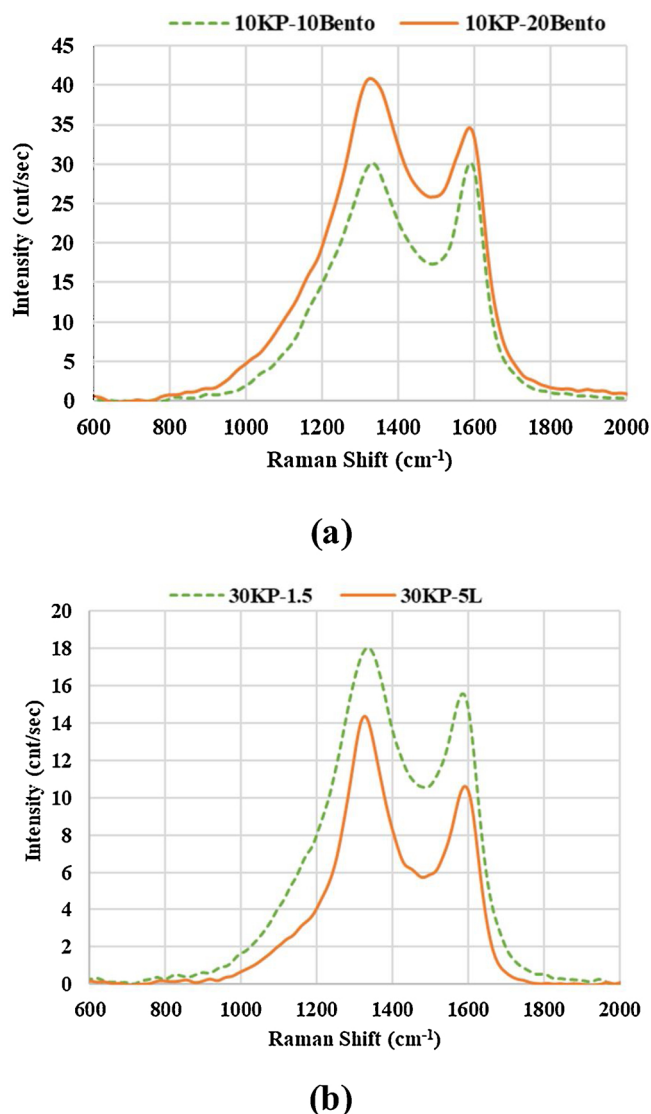


Fig. 4. Raman spectroscopy for different spent catalysts produced from microwave catalytic pyrolysis: (a) 10KP/10Bento and 10KP/20Bento; and (b) 30KP-1.5 L/min and 30KP-5 L/min.

graphitic coke. In addition, our results from heat flow under TGA (Fig. 1) revealed that the exothermic reactions hardly changed the heating behaviour during pyrolysis stage (260–400 °C). Thus, the synergistic effects on increasing microwave heating from catalyst mixture are mainly caused by the type of pyrolysis coke deposited on the catalyst surface. This implies that different catalyst combinations may catalyze different types of reactions, leading to the formation of less oxygenated coke or more graphitic coke.

Table 6 also shows a great decrease on different bands such as GL band, which represents the carbonyl group, GR band, which represents the amorphous carbon, and SL band, which refers to aryl-alkyl ether, by 89, 50 and 35%, respectively, and the R band, which represents C–H on aromatic rings, was eliminated after  $N_2$  flow was increased from 1.5 to 5 L/min. It should also be noted that biochar produced from 30KP-1.5 L/min showed the highest H/C ratio compared to other samples which may be due to the low aromaticity of the biochar (Supplementary material, Table S2). H/C ratio can be used as an indication of the aromaticity of carbon materials, and a higher H/C ratio means less aromaticity [36]. Those compounds mostly contain the C=O group. It was reported that hemicellulose contains much more C=O contained organic compounds than cellulose and lignin, which are released at

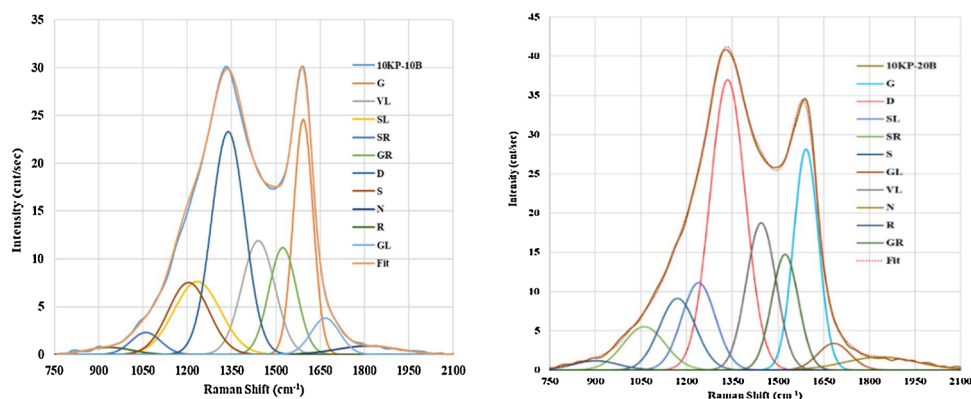


Fig. 5. Deconvoluted peaks of Raman spectra for spent catalysts of 10KP/10Bento and 10KP/20Bento.

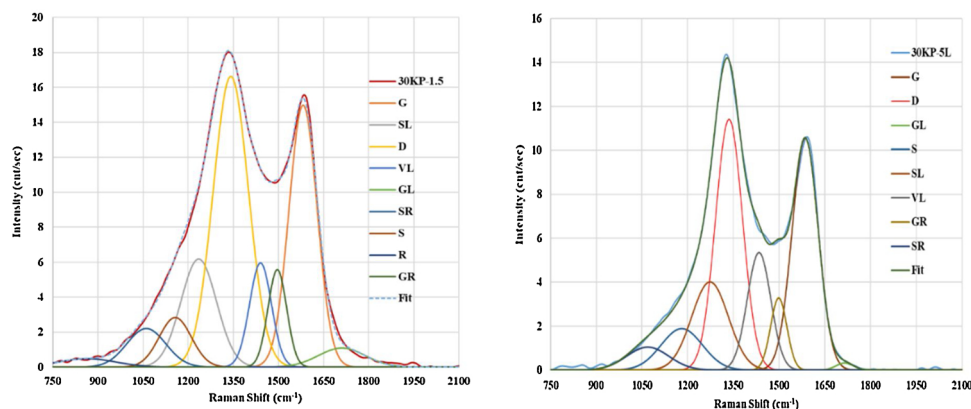


Fig. 6. Deconvoluted peaks of Raman spectra for the spent catalysts of 30KP-1.5 L/min and 30KP-5 L/min.

Table 4

Dielectric properties and microwave heat flow for different materials and spent catalysts.

Samples	Dielectric constant $\epsilon'$	Dielectric loss $\epsilon''$	Penetration depth DP (cm)	Tan $\alpha$	Microwave heat flow <sup>a</sup> (kW/m <sup>3</sup> )
Switchgrass	1.45	0.10	22.54	0.071	52.7
10KP + 10Bento	27.81	35.12	0.29	1.263	18518.3
30KP, 5 L/min N <sub>2</sub>	11.37	14.36	0.45	1.262	7570.8
30KP, 1.5 L/min N <sub>2</sub>	7.01	1.59	3.18	0.227	838.3
K <sub>3</sub> PO <sub>4</sub>	3.25	1.48	2.33	0.455	780.3

<sup>a</sup> Microwave heat flow calculated at room temperature using 750 W microwave power output.

Table 5

Raman bands, band position and bond type for Raman Spectroscopy.

Band name	Band position (cm <sup>-1</sup> )	Description	Bond type
GL	1700	carbonyl group C = O	sp <sup>2</sup>
G	1590	graphite E <sub>2g</sub> <sup>2</sup> , aromatic ring quadrant breathing, alkene C=C	sp <sup>2</sup>
GR	1540	aromatics with 3–5 rings, amorphous carbon structures	sp <sup>2</sup>
VL	1465	methylene or methyl, semicircle breathing of aromatic rings, amorphous carbon structures	sp <sup>2</sup> , sp <sup>3</sup>
D	1340	D band on highly disordered carbonaceous materials, C–C between aromatic rings and aromatics with no less than six rings	sp <sup>2</sup>
SL	1230	aryl – alkyl ether, para-aromatics	sp <sup>2</sup> , sp <sup>3</sup>
S	1185	Caromatic – C <sub>alkyl</sub> , aromatic (aliphatic) ethers, C–C on hydroaromatic rings, hexagonal diamond carbon sp <sup>3</sup> , C–H on b aromatic rings	sp <sup>2</sup> , sp <sup>3</sup>
SR	1060	C–H on aromatic rings, benzene (ortho-disubstituted) ring	sp <sup>2</sup>
R	960–800	C–C on alkanes and cyclic alkanes, C–H on aromatic rings	sp <sup>2</sup> , sp <sup>3</sup>

temperatures of 200–400 °C [27], and may correspond to the two peaks of the DTG at low temperatures (160 and 285 °C) for the spent catalyst of 30KP-1.5 L/min (Fig. 3). Those observations are also supported by the properties of bio-oil produced from 30KP-1.5 L/min under microwave heating, which has a higher pH (by 82%) and lower acid compounds content (by 76%) than bio-oil produced from pure SG, resulting

from condensation and repolymerization of those oxygenated compounds (Table 3). Increasing the N<sub>2</sub> flow rate for 30KP sample under microwave catalytic pyrolysis to 5 L/min removed vapours more rapidly which in turn will reduce the deposition of oxygenated and amorphous coke precursors originated from hemicellulose decomposition. This in turn resulted in a significant decrease in oxygenated and

**Table 6**

Peak areas of the Raman bands corresponding to the coke deposit on different spent catalysts produced from microwave catalytic pyrolysis.

Spent catalyst sample	G	D	D/G	SL	VL	GR	GL
10KP-10Bento	2042	3292	1.61	1164	1664	1316	462
10KP-20Bento	2862	5358	1.87	1543	2294	1622	452
30KP-1.5 L/min	1752	2453	1.40	921	544	435	214
30KP-5 L/min	1133	1268	1.12	607	518	220	24

amorphous coke deposited on the catalyst surface and lowered D/G ratio, compared to 30KP-1.5 L/min. Thus, the microwave heating rate for 30KP-5 L/min sample was remarkably higher than 30KP-1.5 L/min.

While  $K_3PO_4$  inhibited the decomposition of hemicellulose which led to the increase in oxygenated and amorphous coke precursors originated from hemicellulose decomposition, our previous study showed that bentonite and clinoptilolite did not inhibit hemicellulose decomposition [37]. Thus, adding bentonite or clinoptilolite to  $K_3PO_4$  would increase the microwave absorption rate of the sample, resulting in significant decrease in oxygenated and amorphous coke precursors and increase in graphitic coke that can further increase microwave absorption ability of the sample. These findings clearly show that catalyst mixtures increased the microwave heating rate by producing less oxygenated coke and more graphitic coke, which changed the microwave absorption rate compared to the case with a single catalyst. These are also supported by TPO, the measured dielectric properties and calculated microwave heat flow for the spent catalysts as shown in Table 4 and Fig. 4. The spent catalyst for 10KP/10Bento sample showed the highest amount of graphitic coke and the highest calculated microwave heat flow, which also in line with the highest microwave heating rate compared to other spent catalysts samples that contain more deposited oxygenated and amorphous coke on their surfaces.

In summary, coke type plays an important role on determining microwave heating rate and products distribution under microwave catalytic pyrolysis, and these different coke types may be triggered as a result of different catalytic reaction mechanisms. This implies that it is possible to select different catalyst combinations to catalyze different reactions so as to form less oxygenated coke or more graphitic coke. Deposit on catalyst surfaces, the in-situ generated graphitic coke will significantly increase the microwave heating rate. It should be noted that small amount of deposited oxygenated coke on catalyst surfaces can result in a significant decrease in microwave heating rate because of their poor dielectric properties. This explains the data in Tables 1 and 2, where changes in the oxygenated and amorphous carbon affected the microwave heating rate at the pyrolysis stage (260–400 °C) for catalyst mixtures and single catalyst.

#### 4. Conclusion

The catalytic and heating effects of mixtures of different catalysts in biomass catalytic pyrolysis under microwave heating were investigated in a microwave reactor and a TGA. The highest microwave heating rates for torrefaction (110–260 °C) and pyrolysis stages (260–400 °C) were found for 10KP/10Bento sample. It was also found that the catalyst mixtures affected the type of coke deposited on catalyst surfaces which plays an important role on determining the microwave heating rate under microwave catalytic pyrolysis by affecting the dielectric properties of the sample and then microwave absorption. Significant decrease in amorphous and oxygenated coke was found when the catalysts mixtures were applied. Increasing the  $N_2$  flow rate under microwave catalytic pyrolysis for  $K_3PO_4$  resulted in 89% decrease in amorphous and oxygenated carbon which resulted in increase in microwave heating rate and 37% reduction in solid yield. Coke deposit on catalyst surfaces has a greater effect on determining the microwave heating rate and the heating behaviour of the sample than the type of

pyrolysis reactions (endothermic or exothermic). Oxygenated and disordered coke type deposited on catalyst surfaces is responsible in reducing the microwave heating rate, which should be minimized or completely avoided, while the deposited graphitic coke increases the microwave heating rate considerably, which should be further explored in the future as an *in-situ* tool to promote sample heating rate in microwave pyrolysis reactors.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.04.058>.

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